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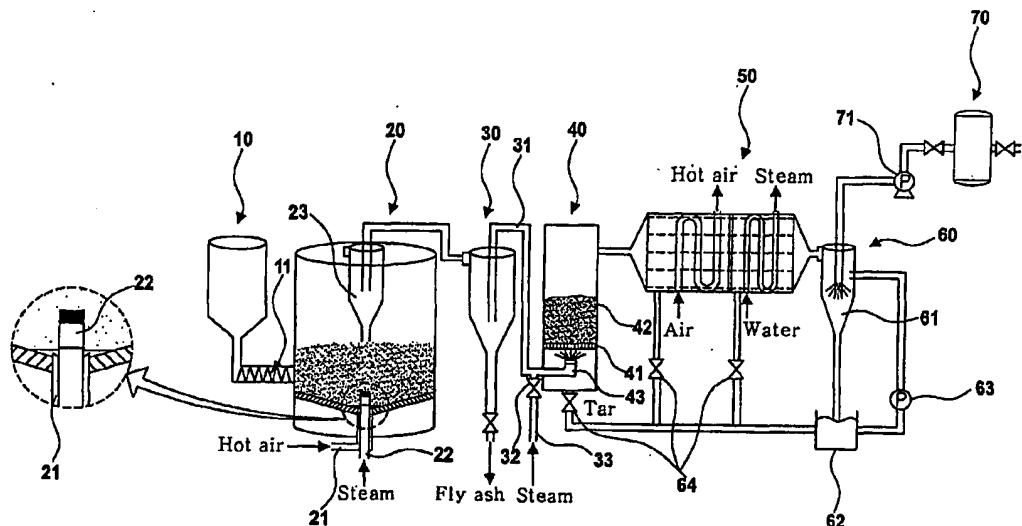
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(54) Title: APPARATUS OF CATALYTIC GASIFICATION FOR REFINED BIOMASS FUEL AT LOW TEMPERATURE AND THE METHOD THEREOF



(57) Abstract: Disclosed is a gasification technique for converting biomass, which is difficult to treat, into clean gas fuel able to be burned in a cogeneration system. The gasification technique includes first stage fluidized-bed catalytic gasification, and second stage gasification of tar and catalytic reforming to convert nitrogen in tar, and HCN in a flammable gas into NH<sub>3</sub>, unlike conventional gasification techniques. In addition, since the temperature of a total gasification process is lower than a melting point of ash, powdery ash is generated and thus easily treated. Also, little heat is released due to the low process temperature, and therefore, a compact reactor may be designed to produce gas having a high calorific value. Further, the generated tar is recovered and reused in other processes, and the gas fuel contains a small amount of ammonia.

WO 2006/031011 A1

**APPARATUS OF CATALYTIC GASIFICATION FOR REFINED BIOMASS FUEL AT LOW TEMPERATURE AND THE METHOD THEREOF**

5                   **Technical Field**

The present invention relates, in general, to gasification techniques for using biomass having a low inorganic ash content and a high nitrogen content as clean fuel in a local heating system of a big city.

10                  In particular, the present invention relates to an apparatus and method for manufacturing a gas fuel via clean gasification of a selectively refined mixture (SOCA: Sludge-Oil-Coal Agglomerates) comprising biomass organic waste, heavy oil, and coal.

15                  As such, the gas fuel obtained after clean gasification is a clean gas fuel usable in gas combustors, such as gas engines, gas turbines, vapor turbine generators, fuel cells, boilers, etc., or in heating devices. In addition, the biomass is organic solid materials, which include industrial waste such as sewage sludge, pulp sludge, etc., living waste such as home waste, excretions, etc., agricultural waste, livestock excretions, or wood chips.

20                  **Background Art**

25                  Generally, gasification techniques have begun to be used to easily prepare gas fuel or synthetic gas from coal in the absence of a catalyst. In recent years, the above techniques have been developed toward entrained gasification and catalytic gasification for fine coal.

30                  While fluidized-bed catalytic gasification, which is combined with fluidized-bed combustion techniques, has been applied to heavy oil reforming, and has been attempted for use in gasification of coal and biomass, methods for high-temperature and clean gasification to produce a minimum of tar are being devised.

35                  Solid fuel is gasified along with reactive materials, such as air, oxygen, or steam, and thus, is converted into a flammable gas, condensed liquid/tar, and solid residue. Generally, although gasification is used to maximally convert solid fuel into gas fuel, it may be limitedly applied in a partial gasification

process. In addition, pyrolysis, which is different from gasification, means thermal decomposition of solids in an inert atmosphere. However, the initial state of gasification is assumed to be devolatilization of pyrolysis. At this time, the fuel is decomposed into char and volatile components. After the 5 devolatilization, a final component distribution of product gas is determined through the secondary reaction between char and volatile gas. In practice, the distribution of the product varies greatly with the gasification methods and the process conditions.

10 In high-temperature gasification, almost all inorganic material contained in coal or sludge is converted into ash or slag. In addition, iron or sodium contained in coal or sludge is volatilized at 900°C or higher, and then sticks on the wall of a heat exchanger. In addition, fuel-nitrogen (fuel-N) is converted into NH<sub>3</sub>, HCN, or N<sub>2</sub>, via gasification, in which the conversion depends on the type of gasification reactor, fuel properties and operation conditions.

15 Since the gasification of coal is typically performed at a high temperature, it requires a lot of energy. The gas thus obtained has a low caloric value, and ashes enter a molten state. Consequently, the system is too large or is complicated. However, when a catalyst able to improve gas composition and 20 operation conditions is used, a gas composition the same as is obtained upon high-temperature gasification in the absence of a catalyst is obtained even at a relatively low temperature, and the conversion of fuel-N is easier. According to some reports, the conversion of fuel-N into NH<sub>3</sub> and HCN is affected by the catalyst and reaction temperature. That is, fuel-N is readily converted into NH<sub>3</sub> in the presence of Fe and Ni catalysts at 900°C or more, while HCN is readily 25 obtained in the presence of a dolomite catalyst at 800°C or more.

30 A gas resulting from gasification typically has a low caloric value. For example, compared to LNG having a caloric value of about 10,000 kcal/Nm<sup>3</sup>, a gas having a low caloric value of 1,100-1,450 kcal/Nm<sup>3</sup> is obtained when gasifying coal having a caloric value of 6,850 kcal/kg.

35 The low-temperature non-catalytic gasification of coal is, in practice, performed at a temperature of not less than a melting point of ash, due to a low conversion rate. However, since the gasification of biomass having lower ash content adopts catalytic gasification, fuel having high quality may be obtained while decreasing the conversion of fuel-N into NO at a low temperature at which ash slagging does not occur.

Further, the above process is applied to gasification of waste having a high caloric value or heavy oil, or to a fuel mixture containing coal. Particularly, waste containing chlorine ion is designed to have a retention time of 2 sec or more at 1200°C or higher to remove it or directly burn it after 5 gasification. In addition, in the case of polymer waste having high quality, a specific gasification process, which produces a fuel having high quality, such as hydrogen, may be proposed.

However, a specific gasification apparatus requires a means for removing and refining large amounts of impurities, such as ash included in a raw 10 material, and generally, also requires a quenching system to produce ash, which is melted by increasing the temperature to achieve high gasification conversion in the absence of a catalyst, into fine slag. Further, a pure oxygen or air separating device for the production of a gas having high caloric value is used, thereby increasing the driving cost or mounting cost. For gasification of a raw 15 material having a low caloric value, a system is installed for indirect heating particularly by an external heat source and pyrolysis through supplying only steam to the system, and is thus used for specific purposes when economy is unimportant.

Hence, the partial oxidation in the absence of a catalyst is 20 disadvantageous because high-temperature air or enriched oxygen must be used to achieve high-temperature gasification. Also, additional fuel is consumed to obtain a product gas (CO and H<sub>2</sub>) having high quality. Further, expensive heat 25 resistant material suitable for high-temperature reactions should be used, and also, the reactor has a short service life. Furthermore, about 2~5% of the free carbon that is produced by high-temperature partial combustion using a fixed-bed reactor is deposited, and the reaction efficiency is gradually decreased, thus requiring additional cost for removing the deposited material.

In the clean solid fuel having less tar or char, circulating low- 30 temperature catalytic gasification, in which organic hydrocarbon and water vapor are converted into a product gas in the presence of an oxide catalyst (MO), may be conducted. Therein, the catalyst is reduced and converted into a pure metal (M). A metal (M) having decreased catalytic activity is reproduced into metal oxide (MO) in a combustor. In addition, the catalytic reaction is conducted at a low temperature of 400-600°C, and a liquid product may be

produced in a very small amount. However, the above gasification is limited to use for waste containing a higher ash content or catalytic poison.

The circulating reforming catalyst generally includes Ni and Co, and preferably, V, Cr, Fe, Cu, Mo, Ag, Cd, La, Ce, or perovskite catalysts, and more preferably, a precious metal having high catalytic efficiency, such as Rh or Ru. In addition, such a catalyst may be affixed to a support formed of oxides of at least two metals selected from among Mg, Ca, Sr, Ba, Al, Ce, Si, Ti, and Zr. However, since these catalysts have low activities due to catalytic poison at a low temperature, they may need to undergo high-temperature reaction or reproduction to be stably used. Consequently, free carbon is deposited on the catalyst, or reacts with the support to form another product. For example, an Ni catalyst reacts at high temperature with alumina, to produce  $\text{NiAl}_2\text{O}_4$ , resulting in decreased catalytic activity. To avoid such a reaction, hexaaluminate ( $\text{MeO}\cdot 6\text{Al}_2\text{O}_3$ ), which has high temperature resistance, may be used as a supporter.

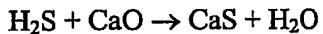
Moreover, liquid waste containing large amounts of solid impurities, such as heavy metals, may be gasified in a supercritical state using a reactor into which a catalyst is loaded. As such, the catalyst, such as Ru, Pd, R, Pt, Au, Ir, Os, Fe, Ni, Ce, or Mn, may be impregnated into titania or zirconia having high temperature resistance, and be driven at 250~600°C under 5~130 MPa. The catalyst used is expensive precious metal, and is thus recovered using a gas-liquid separator to be reused.

A solid-solid catalytic reaction is difficult to perform in practice. Hence, the catalytic gasification of coal, in which an alkali catalytic component is impregnated into coal or a large amount of alkali metal in ash is used, has been initially developed. However, in recent years, as the char gasification reaction of coal was proven usually to be caused by fine volatilization on the surface of particles, attempts have been made to mix a solid catalyst with coal. In the case of sub-bituminous coal having a relatively large amount of volatile material, potassium carbonate is used as a catalyst. As such, the solid material contained in the ash affects the gasification properties. On the whole, a potassium catalyst has a large difference in activity depending on the type of anion combined therewith. In addition, the activity of an iron ion is easily decreased by sulfur, and a nickel ion having low catalytic activity due to

catalytic poison restores the activity at a high temperature at which the poisonous material is desorbed.

Using the catalytic properties, the gasification may be rapidly conducted at a relatively low temperature of 700~850°C in the presence of an optimal catalytic composition, such as  $K_2SO_4 + FeSO_4$ ,  $K_2SO_4 + Ni(NO_3)_2$ , or  $K_2SO_4 + CaCO_3$ . However, a complicated apparatus for melting the remaining ash is necessary due to its low conversion.

Of two-stage gasification methods, air gasification in a cylindrical reactor and water vapor gasification outside of the reactor are conducted at about 850°C, thus obtaining a gas product having a mean caloric value. Limestone is used as a catalyst, in consideration of sulfur poisoning in coal. As such, the reaction is as follows:



Then, the solid materials, for example, CaS, CaO and limestone, may be separated from each other by use of the difference in density in the reactor. The ash and limestone may be separated from each other in the lower portion of the reactor. To this end, however, accurate driving is required due to a complicated reactor and process.

FIG. 1 is a view showing a conventional apparatus for two-stage gasification of biomass at a high temperature in the absence of a catalyst. In a conventional two-stage pyrolysis apparatus of biomass shown in this drawing, a biomass fuel is supplied to a circulating fluidized-bed heating furnace 102 from a fuel hopper 101, and then sequentially passed through a cyclone 103, a char separator 104 and a gas reforming furnace 105, to achieve two-stage pyrolysis. Subsequently, the fuel gas is passed through a pre-heater 106 and then a gas quencher 107, whereby fly ash is collected in a collector 108 and a gas is refined in a refiner 109.

The above apparatus is disadvantageous because first-stage pyrolysis is conducted at 450~850°C, which is not high, in the absence of a catalyst, in consideration of high-temperature volatilization of heavy metal, thus obtaining a low gasification yield and generating excess tar. Hence, a process of reforming tar should be necessary to increase the gasification yield, which is conducted at 1000~1200°C in the absence of a catalyst. Although exhaust flue gas desulfurization is considered for biomass containing a low sulfur content, pollution attributed to high content of phosphorous or fuel-N is not considered,

causing secondary environmental pollution. In particular, the above apparatus has the gas quencher 107 for inhibiting the dioxin conversion by chlorine ions present in the raw material.

5 FIG. 2 is a view showing a conventional apparatus for two-stage catalytic gasification of waste having high quality. Since the waste having low impurities with a high caloric value has a small amount of poisonous material, as shown in FIG. 2, a raw material undergoes first stage partial oxidation and pyrolysis using a fluidized-bed in the absence of a catalyst at about 700~800°C in a fluidized-bed gasifier 110, after which the temperature of the produced 10 flammable gas is decreased to about 300°C. Then, slaked lime is added to fix Cl and S, which are then collected in a cyclone 103 to remove them. The temperature of the flammable gas is increased again after passing through a gas mixer 111 and a combustor 112, and thereafter, second stage tar catalytic reforming is conducted in a gas reformer 113. It is known that an NiO/MoO catalyst is active at 400~500°C, and a catalyst obtained by supporting Ni, Cr and 15 Fe to alumina is active at 800~1000°C. The reference numeral 114 designates a boiler, and the reference numeral 115 designates a gas-holder. Also, parts common to the apparatus shown in FIG. 1 have the same reference numerals.

20 **Disclosure of the Invention**

Technical tasks to be solved by the invention

25 Accordingly, the present invention has been made keeping in mind the above problems occurring in the prior art, and an object of the present invention is to provide a catalytic gasification technique of poison-resistance in a first stage gasification process using a further refined fuel to increase the gasification yield at a low temperature, and then in the gasification of tar and conversion of tar-N and HCN present in a flammable gas into NH<sub>3</sub> in a second stage catalytic reforming process.

30 Another object of the present invention is to provide a gasification technique, using a compact apparatus without the need for a molten ash quenching system, in which the unit calories of the produced gas are increased and ash is formed not in a molten state but as fly ash, by minimizing the content of CO<sub>2</sub> in the gas while decreasing the energy consumption of a reaction system 35 by decreasing the temperature of a total process.

Technical Solution

In order to accomplish the above objects, the present invention provides an apparatus for low-temperature catalytic gasification of a refined biomass fuel, comprising a fuel hopper to momentarily receive refined fuel, and including a screw feeder to quantitatively feed the fuel, provided at the lower portion thereof; a catalytic circulating fluidized-bed gasifier provided in the rear of the fuel hopper, and including a shutter connected to the screw feeder, provided at a middle portion of the gasifier, and a hot air pipe and a steam pipe, provided at a lower portion thereof; a dust collector connected to the catalytic circulating fluidized-bed gasifier via a pipe extending from the upper portion of the catalytic circulating fluidized-bed gasifier to the side wall of the upper portion of the dust collector, to collect fly ash; a catalyst reformer connected to the dust collector via a pipe extending from the upper portion of the dust collector to the lower portion of the catalyst reformer, and including a lower layer of fixed filter adsorbent bed and an upper layer of fluidized catalyst bed; a heat exchanger connected to the catalyst reformer via a pipe extending from the upper portion of the catalyst reformer to the middle portion of the heat exchanger; a tar scrubber disposed in the rear of the heat exchanger, and including a tar scrubbing chamber, a tar-storing bath, and a circulation pump for circulating tar; and a gas-holder disposed in the rear of the tar scrubber.

In addition, the present invention provides a method of low-temperature catalytic gasification of a refined biomass fuel, comprising a fuel supplying step of supplying a refined mixture including biomass organic waste, coal and heavy oil to the middle portion of a gasifier through screw feeder; a catalytic circulating fluidized-bed gasification step of drying, volatilizing, low-temperature catalytic gasifying, and partially burning the fuel using hot air and steam in the presence of a catalyst; a collecting step of collecting fly ash contained in the gas in the previous step; a catalyst reforming step of reforming the gas through a lower layer of filter and reforming tar-nitrogen, aromatic-nitrogen, phosphorous and sulfur through an upper layer; a heat exchanging step of cooling the gas to 200°C or less and transferring condensed liquid to a tar-storing bath; a tar scrubbing step of condensing non-converted tar or non-condensed liquid to be recovered, and gas stripping the condensed liquid; and a gas-holding step of compressing the gas to be stored temporarily.

Advantageous Effects

According to the present invention, the gasification of a fuel which is initiated at a temperature lower than that of a single fuel material may be conducted at a temperature which is further decreased by using a catalyst. 5 Thereby, oxygen consumption required to maintain the operation temperature is decreased, thus a desired fuel may be inexpensively produced. In addition, since the operation temperature of a gasifier is low, little heat is released and a slagging treatment system is not needed, thereby realizing a compact apparatus. In addition, a gas product obtained by using a smaller amount of air in the 10 present invention has the same caloric value as a gas product resulting from conventional gasification using oxygen, therefore generating economic benefits.

The present invention pertains to clean energy producing techniques for converting a highly refined mixture comprising sludge and coal into an inexpensive gas fuel having a high caloric value.

15 The gasification of the refined mixture comprising sludge/coal/oil is initiated, along with a material having a high initiation temperature of gasification, at a temperature lower than that of a single component. Thus, gasification may be performed for a short time, hence achieving rapid gasification. A low ash content and easy control of fly ash at a low 20 temperature make it easier to decrease the size of an apparatus, leading to saved energy and efficient operation. Moreover, since a heavy metal and a salt are present in a very small amount, a combustion post-treatment system is not needed.

25 The gasification adopts a fluidized-bed type which may be driven at a relatively low temperature. Thus, even if the gasification is conducted at 850°C using inexpensive coarse limestone powders or particles which enable gasification at a low temperature, it may exhibit the same effects as conventional gasification at 1100°C or more in the absence of a catalyst.

30 Conventionally, the reformation temperature of a tar reformer is in the range of 1200°C or more, which is higher than a gasification temperature. However, in the present apparatus, the reformation temperature is decreased to 650°C or less, and thus, the reformer of the present invention does not need an additional heat source. Before the catalytic reformation, hydrogen sulfide and phosphorous pentoxide gas acting as a catalyst poison component are fixed to be

removed by the use of caustic lime, thus increasing the reformation of tar and the conversion of fuel-N into NH<sub>3</sub> in the presence of a catalyst.

Although tar, regarded as an unnecessary material, is re-circulated or wasted in a conventional process, in the present invention, unreacted tar, tar generated from the catalytic reformation, and a liquid product formed upon cooling the gas are recovered and then used for other purposes. Typically, additional devices or usage methods are required to re-introduce an undesired liquid component such as tar caused by a conventional coal gasification process into the gasification process or to use it as a liquid fuel. However, in the present invention, since such a component may be used as an agglomerating agent to form an agglomerate, it is not problematic.

#### **Brief Description of the Drawings**

15 FIG. 1 is a schematic view showing a conventional apparatus for two-stage gasification of biomass at a high temperature in the absence of a catalyst;

FIG. 2 is a schematic view showing a conventional apparatus for two-stage catalytic gasification of waste having high quality;

20 FIG. 3 is a view showing an apparatus for two-stage catalytic gasification of a refined biomass fuel, according to the present invention;

FIG. 4 is a view showing the gasification properties of refined sewage sludge fuel in the absence of a catalyst and in the presence of a catalyst; and

FIG. 5 is a view showing the two-stage catalytic gasification characteristics of refined sewage sludge fuel.

25

#### **Best Mode for Carrying Out the Invention**

Reference should now be made to the drawings, in which the same reference numerals are used throughout the different drawings to designate the same or similar components.

30 FIG. 3 is a view showing a catalytic gasification apparatus for use in recovering an energy source in the form of gas from a refined biomass fuel, according to the present invention.

35 The refined biomass fuel, which is a flammable material obtained by selectively separating and recovering an organic solid component from biomass

and coal, along with oil, using an oil agglomeration or floating process, has a non-flammable inorganic material (hereinafter, referred to as 'ash') present in an amount less than 6% based on dried material, and is a solid fuel having high quality with a calorific value of 7,000 kcal/kg or more.

5 The apparatus of the present invention comprises a fuel hopper 10 for receiving fuel, a screw feeder 11 to supply the received fuel to a subsequent device, and a catalytic circulating fluidized-bed gasifier 20 provided in the rear of the fuel hopper 10.

10 The catalytic circulating fluidized-bed gasifier 20 includes a shutter provided at a middle portion thereof and through which the fuel is supplied from the screw feeder 11.

15 In addition, the catalytic circulating fluidized-bed gasifier 20 has a hot air pipe 21 and a steam pipe 22 disposed in a conical lower portion thereof. As such, the hot air pipe 21 is positioned at the same level as that of the conical lower portion, and the steam pipe 22 is positioned such that its end is protruded to a height of 15~30 cm apart from the lower portion.

At the upper portion of the catalytic circulating fluidized-bed gasifier 20, a small cyclone 23 may be further provided.

20 A dust collector 30 is provided in the rear of the catalytic circulating fluidized-bed gasifier 20, and a pipe extending from the upper portion of the catalytic circulating fluidized-bed gasifier 20 is connected to the side wall of the upper portion of the dust collector 30. The dust collector 30 functions to collect fly ash in the gas in the lower portion thereof. In addition, a catalyst reformer 40 is provided in the rear of the dust collector 30, and a pipe 31 extending from the upper portion of the dust collector 30 is connected to the lower portion of the catalyst reformer 40.

25 The catalyst reformer 40 has a fixed filter adsorbent bed 41 disposed in the lower portion thereof, and a fluidized catalyst bed 42 formed on the fixed filter adsorbent bed 41.

30 The fixed filter adsorbent bed 41, which is a cartridge type, may include a mixture comprising an asbestos filter, particles of alkali earth metal oxide and powdery particles of alkali metal salt.

35 The pipe 31 extending from the upper portion of the dust collector 30 is provided with a valve 32 at an intermediate position thereof that communicates with a steam pipe 33, and the pipe 31 communicates with a steam sprayer 43

disposed at the lower portion of the fixed filter adsorbent bed 41 of the catalyst reformer 40.

5 In order to prevent liquid from condensing in the gas pipe extending from the cyclone 30 to the catalyst reformer 40, super-heated steam is fed into the gas pipe through the steam pipe 33 so that the gas pipe discharges the super-heated steam into the catalyst reformer 40 along with the gas to cause the remaining tar to be further gasification reformed.

10 In addition, a heat exchanger 50 is provided in the rear of the catalyst reformer 40. Also, a tar scrubber 60 is provided after the heat exchanger 50, and includes a tar scrubbing chamber 61, a tar-storing bath 62 disposed at the lower portion thereof, and a circulation pump 63 for circulating tar. The tar-storing bath 62 communicates with a lower pipe of each of the catalyst reformer 40 and the heat exchanger 50 via individual tar valves 64 to collect the generated tar from the catalyst 40 and the heat exchanger 50.

15 Further, a gas-holder 70 is provided in the rear of the tar scrubber 60, and a fuel gas-storing pump 71 is disposed between the tar scrubber 60 and the gas-holder 70.

Hereinafter, a method of manufacturing clean gas using the apparatus of the present invention is described.

20 A refined fuel mixture, which is supplied through a screw feeder 11 from a fuel hopper 10, undergoes drying, volatilization, low-temperature catalytic gasification, pyrolysis gasification and partial burning, by air or oxygen and water vapor fed via a hot air pipe 21 and a steam pipe 22 in a catalytic circulating fluidized-bed gasifier 20. Unreacted fuel comes into contact with air or oxygen at the conical lower end of the gasifier, and thus, is completely burned.

25 The ratio of air or oxygen supplied into the catalytic circulating fluidized-bed gasifier 20 is about 0.3~0.7 based on the amount of air required for theoretical complete combustion of the refined fuel mixture, and water vapor is fed at a volume ratio of 0.5~10 times that of air. The fluidized catalyst for gasification in the catalytic circulating fluidized-bed gasifier 20 includes natural limestone, lime magnesite, or caustic lime, an alkali earth metal such as calcium, magnesium or barium and oxides thereof, an alkali metal such as potassium and oxides thereof, alumina, or mixtures thereof, each of which is provided in the form of particles or coarse powders suitable for fluidization. By using the catalyst, the gasification is

conducted at a maximal temperature of 900°C or less by high-speed operation, for example, for a gas retention time of 2~4 sec.

Preferably, partial oxidation and low-temperature catalytic pyrolysis are simultaneously conducted at 850°C or less. Upon partial oxidation for feeding a 5 heat source to a system, most gasification uses oxygen at a high temperature. However, in a novel process, even if a fuel having high quality reacts with air serving as a fuel oxidant at a relatively low temperature, the gas may be produced to have the same caloric value as that of a conventional process using oxygen. As such, air is sprayed from the lowermost portion of the gasifier, whereby the 10 lowermost portion of the gasifier has excessive oxygen for complete combustion of unreacted flammable material.

In addition, a small cyclone 23 is provided to the upper portion of the catalytic circulating fluidized-bed gasifier 20 to efficiently collect scattered catalyst or fuel agglomerate such as unreacted material and heavy tar, which is 15 then re-circulated to the catalytic circulating fluidized-bed gasifier 20, thus completing the gasification.

In the cyclone 30, a small amount of fly ash may be efficiently collected and removed.

The catalyst reformer 40 has a two-layered structure, including a lower 20 layer of cartridge type fixed filter adsorbent bed 41 and an upper layer of fluidized catalyst bed 42.

In the fixed filter adsorbent bed 41, fine fly ash is removed via an asbestos filter, and sulfur and phosphorous poisoning are chemically adsorbed and removed using potassium oxide and sodium carbonate as an adsorbent. Also, a 25 detoxification filter may be recycled or replaced after being used for a predetermined period. For example, hydrogen sulfide (H<sub>2</sub>S) generated upon gasification reacts with CaO and is converted into CaS, which is then adsorbed. Also, a vapor compound such as PH<sub>4</sub>-halogen reacts with Na<sub>2</sub>CO<sub>3</sub> to produce NaPO<sub>3</sub>, which is then chemically adsorbed. A phosphorous component is 30 converted into P<sub>x</sub>H<sub>y</sub>S<sub>y</sub>Halogen<sub>8</sub> ( $\alpha=1\text{-}7$ ,  $\beta=0\text{-}5$ ,  $\gamma=0\text{-}7$ ,  $\delta=0\text{-}7$ ) to be chemically adsorbed. Each of P<sub>x</sub>S<sub>y</sub> compounds, resulting from the gasification, reacts with a chemical adsorbent suitable therefor or a calcium salt to be chemically adsorbed.

The fluidized catalyst of the fluidized catalyst bed 42 functions to decompose tar by gasification and convert aromatic nitrogen or HCN into an 35 alkane or alkene compound and NH<sub>3</sub>. The usable reformation catalyst includes a

single metal, such as Ni, Fe, Co, Mo, Mn, Zr, Ti, Ce, Ru, Rh or Pt, and oxides thereof, or mixtures thereof. Such a catalyst is preferably used at 650°C or less.

5 The heat of reformed gas is exchanged by using the heat exchanger 50 to cool the gas to 200°C or less, and the condensed liquid is transferred in the tar-storing bath 62. As such, air or oxygen and water used in the gasification may serve as a cooling medium for heat exchange, and then be converted into hot air and steam. Moreover, the heat exchanger 50 may increase the energy efficiency if a metal heat exchanger made of a high-temperature material is used.

10 The non-converted tar or non-condensed liquid in the catalyst reformer 40 is condensed in the tar scrubber 60, and then recovered in the tar-storing bath 62. In this case, to increase the recovery efficiency of dust and tar, condensed liquid at 150°C or less is re-transferred to the upper portion of the tar scrubber 60 through the tar circulating pump 63, thus conducting gas stripping.

15 The resultant clean gas fuel is compressed and then stored temporarily in the gas-holder 70.

A better understanding of the present invention may be obtained through the following examples which are set forth to illustrate, but are not to be construed as the limit of the present invention.

20 Example 1: Improvement Of Gas Generation Efficiency By Catalytic Gasification

25 For gasification of SOCA (Sludge-Oil-Coal Agglomerates) in the presence of a catalyst mixture comprising  $Fe_2O_3$  and CaO, the catalyst mixture and SOCA were uniformly mixed at a weight ratio of 3.4:1 under operation conditions similar to gasification in the absence of a catalyst, thus obtaining a gas product. The state of the product is shown in FIG. 4. The gasification in the presence of the catalyst mixture was initiated at 230°C, which was considerably lower than 560°C required for gasification in the absence of a catalyst. In addition, compared to gasification in the absence of a catalyst, CO conversion was lower, and more hydrocarbons were generated. In particular, almost all hydrocarbons generated were confirmed to be methane gas. In the gasification in the absence of a catalyst, hydrocarbons were generated at 850°C or more, and CO was generated at 1050°C or more. However, when using a catalyst mixture, CO and hydrocarbon were mainly generated at about 500°C. Further, CO was maximally generated at 850°C. Thereby, gasification was completed in a short time. After the gasification in the presence of the catalyst mixture, unreacted

char was present in an amount of about 0.35%, which was superior to the about 11.31% char remaining after conventional gasification at 1050°C for 2 hr in the absence of a catalyst.

5                   Example 2: Less Generation Of Tar and Fuel-N Pollutant By Two-Stage Catalytic Gasification

As shown in FIG. 5, when a CaO catalyst, which is an oxide of an alkali earth metal, was used in the first stage gasification and an NiO catalyst was used in the second stage catalytic reformation, CO was similarly generated but a slightly larger amount of hydrocarbon was generated, compared to gasification 10 using only CaO as the first stage catalyst. Thereby, the reaction was completed in a shorter time. However, as is apparent from Table 1 below, in the case where calcium oxide was used as a first stage catalyst and NiO or MnO<sub>2</sub> was used as a second stage catalyst, the generation of tar, NH<sub>3</sub> and HCN was remarkably lower than when using only a first stage catalyst. It was considered that tar was 15 reformed and fuel-N was converted into N<sub>2</sub>. In addition, the MnO<sub>2</sub> catalyst was inferior in tar reformation to the NiO catalyst, by which fuel-N was converted not into ammonia but into HCN. Thus, the NiO catalyst exhibited superior fuel-N reformation performance as a second catalyst.

20                   [TABLE 1]  
Conversion Of Tar and Fuel-N By Using Two-Stage Catalysts

Catalyst	Conversion (%)	Tar (%)	NH <sub>3</sub> (%)	HCN (%)	Flammable Gas Composition After Gasification for 45 min (ppm)					
					CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>
1 <sup>st</sup> :CaO 2 <sup>nd</sup> : x	99.08	3.385	0.889	0.656	14,805	209	12	76	223	4,670
1 <sup>st</sup> :CaO 2 <sup>nd</sup> :NiO	99.90	0.123	0.278	0.045	14,429	305	4,974	6,223	4,228	367
1 <sup>st</sup> :CaO 2 <sup>nd</sup> :MnO <sub>2</sub>	99.84	0.703	0.465	0.164	15,766	12,134	46	408	2,102	1,263

**Claims:**

1. An apparatus for low-temperature catalytic gasification of a refined biomass fuel, comprising:

5 a fuel hopper (10) to momentarily receive refined fuel and including a screw feeder (11) to quantitatively supply the fuel, provided at a lower portion thereof;

10 a catalytic circulating fluidized-bed gasifier (20) provided in the rear of the fuel hopper (10), and including a shutter connected to the screw feeder (11), provided at a middle portion of the gasifier, and a hot air pipe (21) and a steam pipe (22), provided at a lower portion of the gasifier;

15 a dust collector (30) connected to the catalytic circulating fluidized-bed gasifier (20) via a pipe extending from an upper portion of the catalytic circulating fluidized-bed gasifier (20) to a side wall of an upper portion of the dust collector (30), to collect fly ash;

a catalyst reformer (40) connected to the dust collector (30) via a pipe extending from the upper portion of the dust collector (30) to a lower portion of the catalyst reformer, and including a lower layer of fixed filter adsorbent bed (41) and an upper layer of fluidized catalyst bed (42);

20 a heat exchanger (50) connected to the catalyst reformer (40) via a pipe extending from the upper central portion of the catalyst reformer (40) to a middle portion of the heat exchanger;

25 a tar scrubber (60) disposed in the rear of the heat exchanger (50), and including a tar scrubbing chamber (61), a tar-storing bath (62), and a circulation pump (63) for circulating tar; and

a gas-holder (70) disposed in the rear of the tar scrubber (60).

30 2. The apparatus according to claim 1, wherein the catalytic circulating fluidized-bed gasifier (20) further includes a small cyclone (23) provided in the upper portion thereof.

35 3. The apparatus according to claim 1, wherein the catalyst reformer (40) further includes a steam sprayer (43) provided at a lower portion of the fixed filter adsorbent bed (41).

4. The apparatus according to claim 1, wherein the fixed filter adsorbent bed (41) is a cartridge type, and includes an asbestos filter, particles of alkali earth metal oxide, and particles of an alkali metal salt, mixed together.

5 5. The apparatus according to claim 1, wherein the tar-storing bath (62) communicates with a lower pipe of each of the catalyst reformer (40) and the heat exchanger (50) via tar valves (64) thereof, to collect the generated tar.

10 6. A method of low-temperature catalytic gasification of a refined biomass fuel, comprising:

a fuel supplying step of supplying a refined mixture including biomass organic waste, coal, and heavy oil to a middle portion of a gasifier using a screw feeder;

15 a catalytic circulating fluidized-bed gasification step of drying, volatilizing, low-temperature catalytic gasifying, and partially burning the fuel using hot air and superheated steam in the presence of a catalyst;

a collecting step of collecting fly ash in the gas generated in the catalytic circulating fluidized gasification step;

20 a catalyst reforming step of reforming the gas through a lower layer of fixed adsorbent bed and reforming tar-nitrogen, aromatic-nitrogen, phosphorous and sulfur through an upper layer of fluidized catalyst bed;

a heat exchanging step of cooling the gas to 200°C or less and transferring condensed liquid to a tar-storing bath;

25 a tar scrubbing step of condensing non-converted tar or non-condensed liquid to be recovered, and gas stripping the condensed liquid; and

a gas-storing step of compressing the gas to be stored temporarily.

30 7. The method according to claim 6, wherein the catalyst used in the catalytic circulating fluidized-bed gasification step is selected from the group consisting of natural limestone, lime magnesite, caustic lime, an alkali earth metal including calcium, magnesium or barium and oxides thereof, an alkali metal including potassium and oxides thereof, alumina, and mixture thereof, each of which is provided in particles or course powders suitable for fluidization.

8. The method according to claim 6, wherein the catalytic circulating fluidized-bed gasification step further comprises re-circulating a scattered catalyst or fuel agglomerate to the catalytic circulating fluidized-bed gasifier (20) through a small cyclone (23).

5

9. The method according to claim 6, wherein the catalyst reforming step further comprises spraying steam onto the lower portion of the fixed adsorbent bed (41) to accelerate reformation and prevent the pipe from clogging, so that a reformation temperature is 650°C or less.

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10. The method according to claim 6, wherein the catalyst reforming step comprises converting hydrogen sulfide into CaS and phosphorous into  $P_\alpha H_\beta S_\gamma Halogen_\delta$  ( $\alpha=1-7$ ,  $\beta=0-5$ ,  $\gamma=0-7$ ,  $\delta=0-7$ ), to be chemically adsorbed into the fixed adsorbent bed (41).

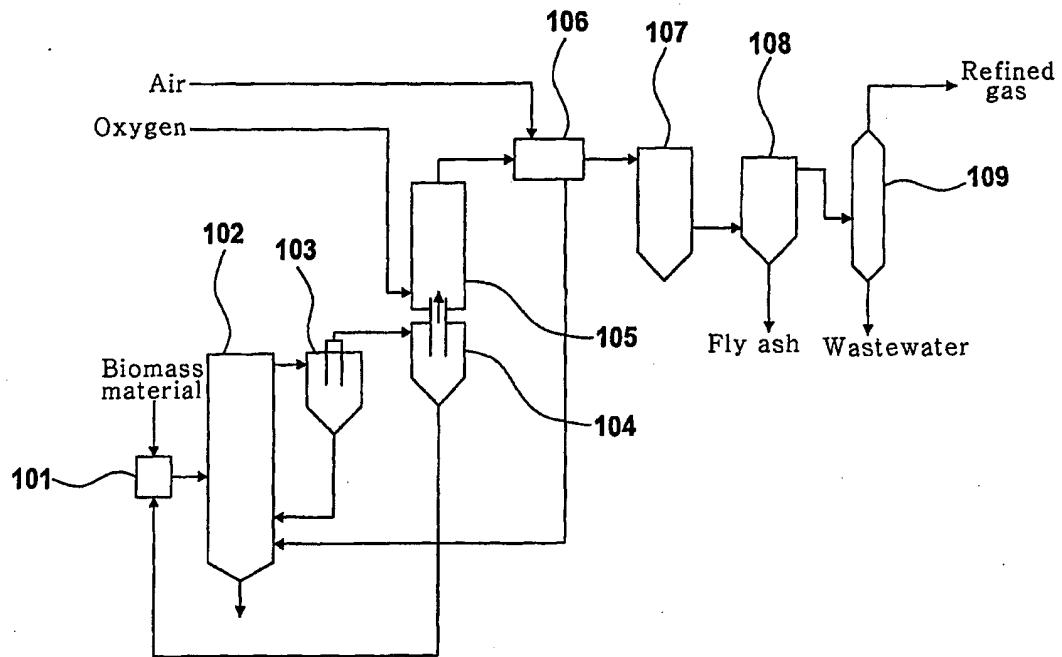
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11. The method according to claim 6, wherein the fluidized catalyst of the fluidized catalyst bed (42) used in the catalyst reforming step is a single metal, including Ni, Fe, Co, Mo, Mn, Zr, Ti, Ce, Ru, Rh or Pt, and oxides thereof, or mixtures thereof, which functions to decompose tar by gasification and convert aromatic-nitrogen or HCN into an alkane compound or an alkene compound and NH<sub>3</sub>.

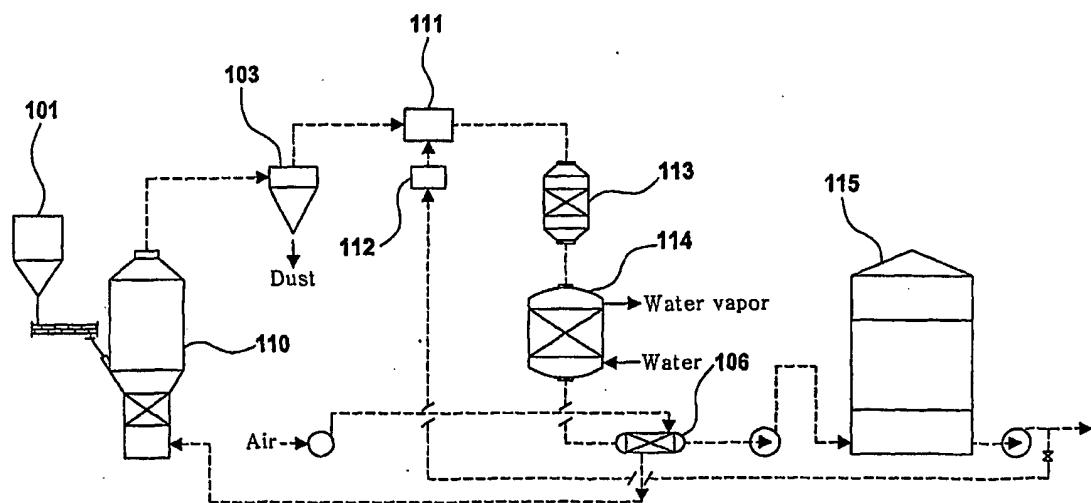
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1/4

【Fig. 1】

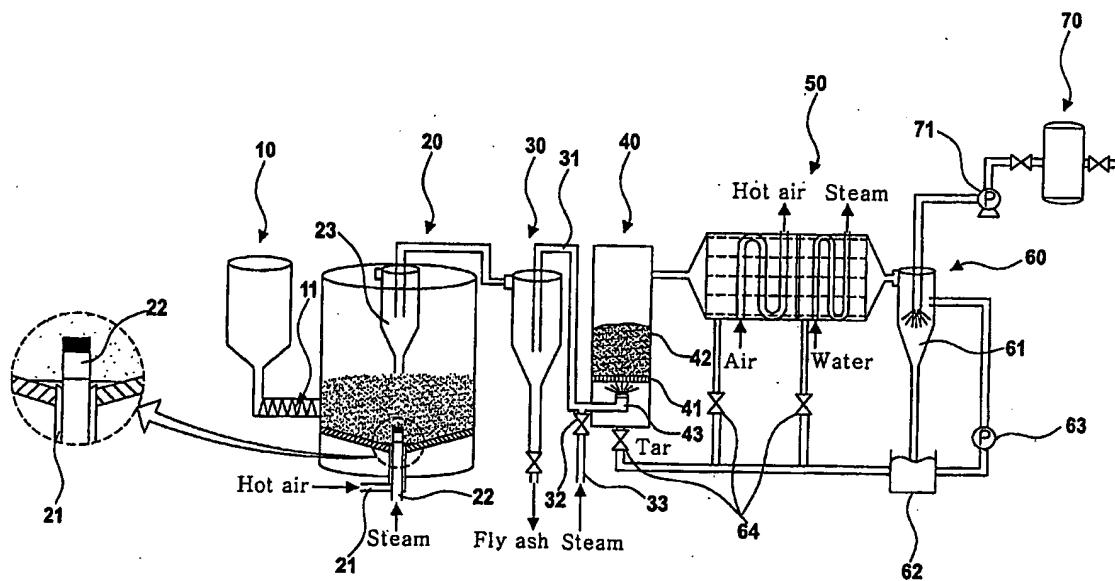


【Fig. 2】



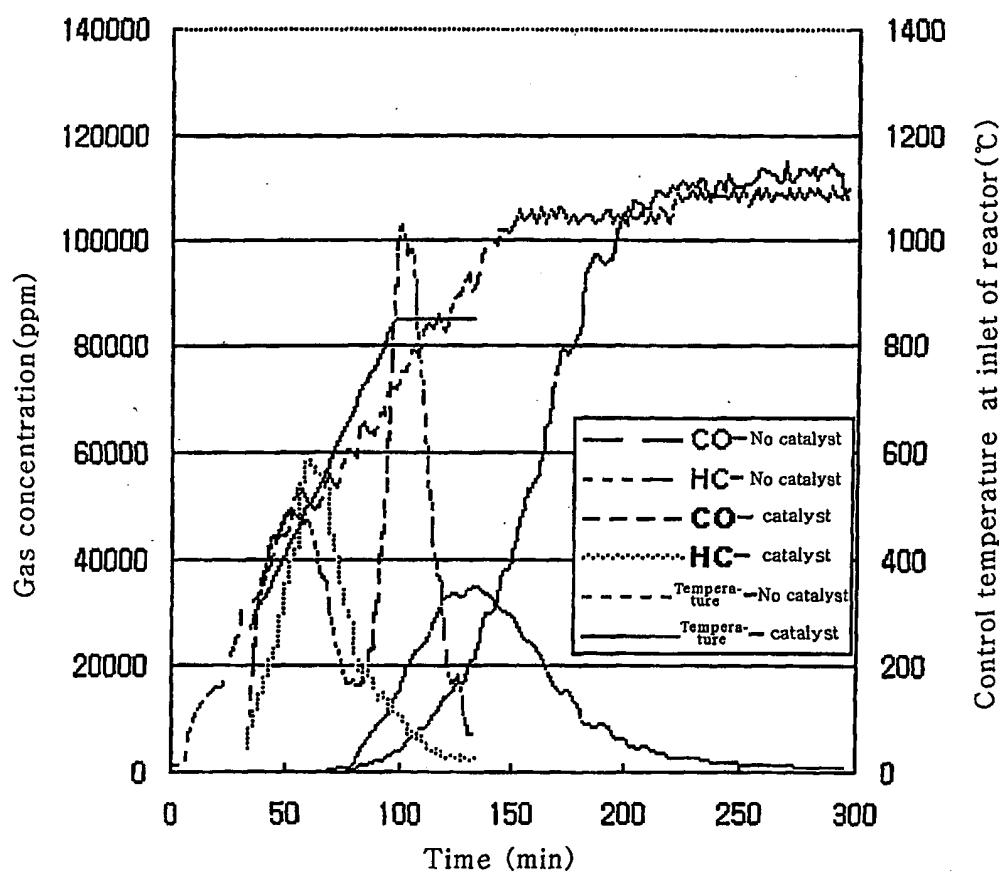
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[Fig. 3]



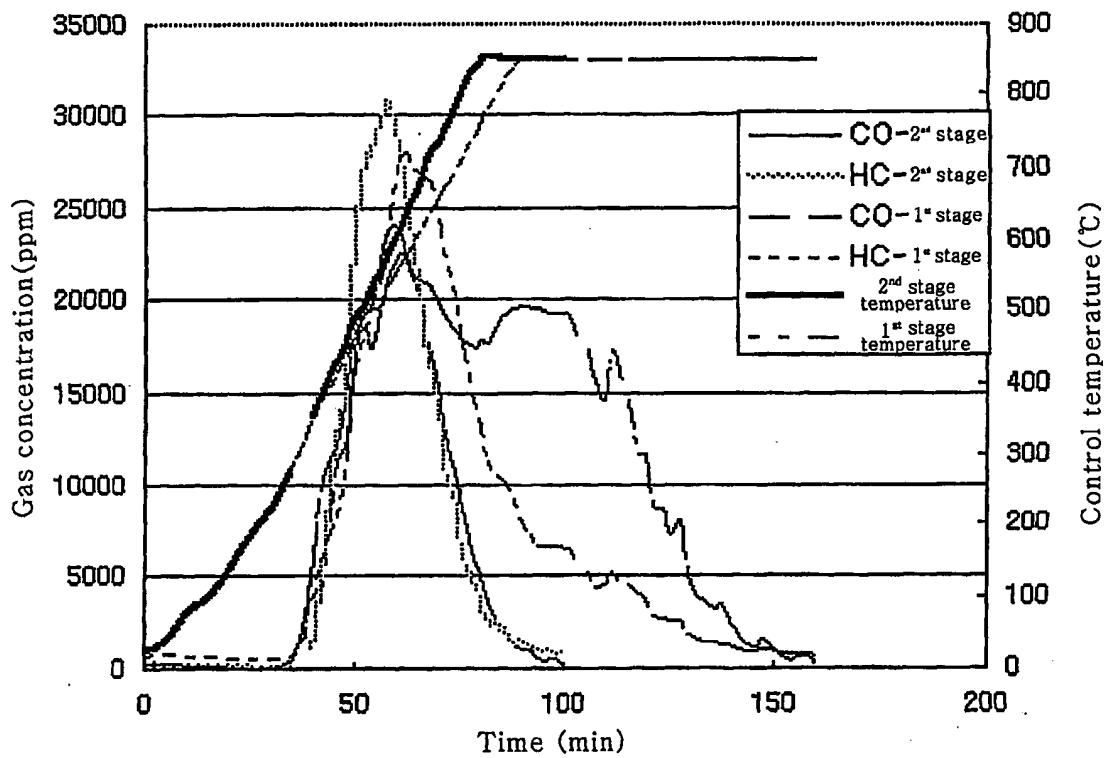
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【Fig. 4】



4/4

[Fig. 5]



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/KR2005/001808

## A. CLASSIFICATION OF SUBJECT MATTER

## IPC7 C10G 1/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
Korean patents and applications for inventions since 1975: IPC C10GElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
Delphion and keywords: gasification, catalyst, biomass and similar terms

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 2004149556 A2 (NISHINIPPON ENVIRONMENTAL ENERGY CO INC) 27 May 2004; abstract	1-11
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A	WO 8904354 A1 (DANSK TERMO INDUSTRI A/S) 18 May 1989	1-11
A	WO 9630464 A1 (UNIVERSITY OF HAWAII) 3 October 1996	1-11

 Further documents are listed in the continuation of Box C. See patent family annex.

- \* Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "&" document member of the same patent family

Date of the actual completion of the international search  
24 AUGUST 2005 (24.08.2005)

Date of mailing of the international search report

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

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